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## (54) A PROCESS FOR THE PREPARATION OF STABLE POLYISOCYANATES WHICH CONTAIN BIURET GROUPS

(71) We, BAYER AKTIENGESELLSCHAFT, formerly Farbenfabriken Bayer Aktiengesellschaft, a body corporate organised under the laws of Germany, of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the preparation of stable liquid polyisocyanates which contain biuret groups.

It is known that polyisocyanates which have a biuret structure can be obtained by the action of water on polyisocyanates. The disadvantage of this process is the formation of substantial quantities of gaseous carbon dioxide.

It is also known that polyisocyanates which have a biuret structure can be obtained by the reaction of primary monoamines with diisocyanates, the monoisocyanate corresponding to the monoamine being split off in the process. This process has the disadvantage in that formation of the monoisocyanate, which is usually highly toxic, cannot be eliminated where necessary.

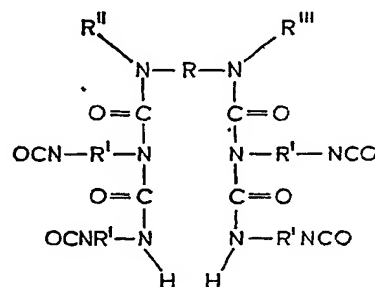
According to British Patent Specification No. 1,078,390, biurets are formed directly from primary diamines and diisocyanates by carrying out this reaction in solvents whose boiling point is below the boiling point of the diisocyanate used, e.g. in chloroform. The disadvantage of this process is that the solvents must be removed by distillation after the reaction. Direction reaction of the diamines mentioned in the examples with the diisocyanates described in the absence of solvents is not possible, because the polyureas, which are formed immediately and which are

insoluble in the isocyanate, prevent further action on the isocyanate.

It has now been found that amines can be reacted directly with diisocyanates, if instead of the above mentioned primary amines, the corresponding secondary amines are used. When reacting diisocyanates with secondary amines, isocyanates which have a biuret structure can be obtained without the formation of the unwanted monoisocyanate.

According to the present invention there is provided a process for the preparation of liquid polyisocyanates which contain biuret groups which comprises reacting amines and polyisocyanates, in which the polyisocyanates are reacted at a temperature of from 80 to 200°C with secondary amines at an NCO/NH ratio of from 4:1 to 100:1.

The special advantage of this process is that the NCO functionality of the biuret polyisocyanate obtained can be determined in advance by the choice of amine component. Thus for example tetraisocyanates having the following general formula:

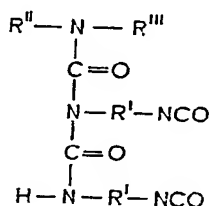


can be obtained from dissecondary diamines and diisocyanates. In the above formula,

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- R represents e.g. a C<sub>2</sub> to C<sub>8</sub> alkylene radical, an arylene radical or a polyarylene radical which contains short chain alkylene groups or hetero atoms as bridging members;
- 5 R' represents the divalent hydrocarbon radical corresponding to the diisocyanate;
- R'' and R''' may be the same or different and represent C<sub>1</sub> to C<sub>4</sub> alkylene radicals which may form a heterocyclic ring together with
- 10 a —N—R—N group, or they may represent an aryl or aralkyl group.

Difunctional isocyanates having the following formula:



- 15 in which

R', R'' and R''' have the meanings indicated above and R'' and R''' may form a heterocyclic ring together with —N—,

- 20 may be obtained from secondary monoamines and diisocyanates.

- By reacting diisocyanates with a mixture of secondary diamine and monoamine or a mixture of secondary monoamine and water, the NCO functionality can be adjusted to intermediate values during the process of preparation.

- When preparing the biuret-containing polyisocyanates by the process according to the invention, the amines which serve as starting materials are used in a proportion corresponding to an NCO/NH ratio of from 4:1 to 100:1, preferably from 6:1 to 40:1. As a rule, the isocyanate is first introduced into the reaction vessel and the amine is added at a temperature of from 80 to 200°C, preferably from 130 to 170°C, at such a rate that the temperature of the preheated isocyanate rises by about 20°C. The amine immediately goes into solution and biuret formation is achieved quantitatively within a short time via intermediate stages which are not isolated. Solid amines may be added in the form of a fine powder, whereas gaseous amines may be passed into the liquid as a stream. The process is so easy to handle that preparation of the biurets may also be carried out continuously.

- For a continuous process, the amine and the isocyanates are supplied from separate containers and intimately mixed before being introduced into heatable reaction tubes. After a short time of stay in the reaction tube, the mixture of isocyanate and biuret leaves the

tube. Since the heat of reaction can easily be controlled, the process may also be carried out adiabatically.

In the process according to the invention, the polyisocyanates containing biuret groups are generally obtained in the form of solutions in the biuret-free polyisocyanate which is used as starting material.

The following are examples of secondary monoamines which may be used in the process according to the invention: N-methyl aniline, N-ethyl aniline, diphenylamine, dibenzylamine, N-methyl naphthylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, pyrrolidine, piperidine and morpholine.

The following are examples of suitable bis-secondary diamines which may be used for the process according to the invention: N,N' - diethyl - 4,4' - diamino - diphenylmethane, N,N' - diethyl - 2,4 - tolylenediamine, N,N' - diethyl - 2,6 - tolylene diamine, N,N' - diethylated aliphatic diamines such as N,N' - diisopropyl ethylene diamine and piperazine.

Suitable polyisocyanates for the process according to the invention are especially diisocyanates such as tetramethylene diisocyanate, hexamethylene diisocyanate, *m*-xylylene diisocyanate, *p*-xylylene diisocyanate, 4,4'-dimethyl-1,3-xylylene diisocyanate, cyclohexylene-1,4-diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, *m*-phenylene diisocyanate, *p*-phenylene diisocyanate, tolylene-2,4- and -2,6-diisocyanate, 1 - benzyl - phenylene - 2,6-diisocyanate, 2,6-diethyl-phenylene-1,4-diisocyanate, diphenylmethane-4,4'-diisocyanate, 3,3' - dimethoxy - diphenylmethane - 4,4'-diisocyanate and naphthylene-1,5-diisocyanate. Trifunctional and higher functional polyisocyanates may also be used, e.g. 2,4,6-triisocyanatotoluene or polymethylene-polyphenylpolyisocyanate obtained by aniline-formaldehyde condensation followed by phosgenation. Isocyanates which contain carbodiimide, uretonimine or isocyanurate groups may also be used. Mixtures of the above mentioned isocyanates may also be used. In addition, reaction products of polyhydric alcohols with polyvalent isocyanates may be used, and polyisocyanates of the type mentioned e.g. in German Patent Specifications No. 1,022,789 and 1,027,394 are also suitable examples.

The polyisocyanates containing biuret groups prepared by the process according to the invention and their solutions in polyisocyanates which are free from biuret groups are valuable starting materials for the production of polyurethane foam resins by the isocyanate polyaddition process.

The present invention, therefore, also relates to the use of the biuret-containing polyisocyanates prepared by the process according to the invention, as isocyanate components for the production of polyurethane foam resins by the isocyanate polyaddition process.

The biuret-containing polyisocyanates are

preferably used for the production of hard, semihard and soft polyurethane foams, and in particular they are advantageously used in the process of foaming in the mould.

5 The last mentioned process is characterised in that the reaction of polyols, polyisocyanates and additives takes place in closed moulds the internal capacity of which is 1/10th to 9/10th of the volume which the foamed  
10 product would take up if expanded in an open mould, the temperature of the internal surface of the mould being at least 20°C lower than the maximum temperature occurring inside the reaction mass during the reaction.

15 This process is based on the finding that the distribution of density over the cross-section of foam products produced by foaming the mixtures described in closed moulds with restricted space for expansion, is a function of the temperature gradient which  
20 becomes established between the surface of the moulding and its core in the course of the reaction. This temperature gradient is obtained from the maximum temperature inside the mass which is being foamed in the mould and the given temperature of the internal surface of the mould.

This maintenance of a temperature gradient between the surface and the core of the foamed  
30 material, which is a characterising feature of the process, results in the finished foam product having massive, dense surfaces, with the density decreasing from the surfaces to the centre, this decrease in density being greater,  
35 the greater the temperature difference between the surfaces and the core. Certain properties, such as the resistance to heat distortion, the rigidity and resistance to bending, are thus considerably improved as compared with these  
40 properties in similar foams which have a uniform density.

The ratio of the volume (V) available to the foaming material for expansion in the closed mould to that volume (Vo) which would  
45 be taken up by the foam if expanded in an open mould should be at least 9:10 and preferably 8:10 to 1:10 (compression factor

$$\left( \frac{V_o}{V} \right)$$

at least 1.1 and preferably 1.25 to 10).

50 Both for foaming in the mould and for producing freely expanded polyurethane foams, any compounds known in polyurethane chemistry which contain hydrogen atoms that are reactive with isocyanate groups, are suitable for use as reactants for the polyisocyanates which contain biuret groups. Any of  
55 the activators, emulsifiers, blowing agents and flame retarding substances, for example, commonly used in polyurethane chemistry may be  
60 used as additives.

Any compounds which contain hydroxyl

and/or carboxyl groups may be used as reactants for the polyisocyanates or polyisocyanate solutions used according to the invention. Suitable polyhydroxyl compounds are  
65 especially the low molecular weight polyhydric alcohols and higher molecular weight polyesters, polyethers, polythioethers, polyacetals, polycarbonates and polyether amides which contain several hydroxyl groups, of the type  
70 known *per se* for the production of cellular polyurethanes.

Suitable hydroxy polyesters include e.g. reaction products of polyhydric alcohols with polybasic acids, a wide variety of which are  
75 known in the art. Instead of free carboxylic acids, however, the corresponding polycarboxylic acid anhydrides, polycarboxylic acid esters or mixtures of these compounds may be used for the preparation of the hydroxy  
80 polyesters. The polycarboxylic acids may be aliphatic, cycloaliphatic, aromatic and heterocyclic compounds, and these may be substituted and/or unsaturated. The following are mentioned as specific examples: succinic acid,  
85 adipic acid, sebacic acid, phthalic acid, isophthalic acid, phthalic acid anhydride, maleic acid, maleic acid anhydride, monomeric, dimeric and trimeric fatty acids and dimethyl terephthalates. Suitable polyol components  
90 include e.g. ethylene glycol, propylene glycol-(1,3), butylene glycol-(1,4), butylene glycol-(2,3), glycerol, trimethylol ethane, pentaerythritol, mannitol and sorbitol, methyl glycoside, polyethylene glycols, polypropylene  
95 glycols and polybutylene glycols. Polyesters which contain terminal carboxylic groups are also suitable for the reaction with the polyisocyanates.

Suitable hydroxy polyethers are those of  
100 known type, and they may be prepared e.g. by the polymerisation of epoxides such as ethylene oxide, propylene oxide, butylene oxide, styrene oxide or epichlorohydrin, optionally with starting components which contain  
105 reactive hydrogen atoms, such as alcohols or amines, e.g. glycerol, trimethylol propane, ethylene glycol, ammonia, ethanolamine or ethylene diamine. Sucrose polyethers may also  
110 be used.

Examples of polyhydroxyl compounds which are suitable for the reaction with the polyisocyanates which contain biuret groups are described e.g. in Saunders-Frisch "Polyurethanes, Chemistry and Technology",  
115 Volumes I and II, Interscience Publishers 1962 and 1964 (pages 32 *et seq* of volume I and page 5 and pages 198 *et seq* of volume II) and in Kunststoff-Handbuch, Volume VII, Vieweg-Hochten, Publishers Carl-Hanser-Verlag, Munich 1966, e.g. on pages 45 to 71. Epoxy resins, hydrogenation products of  
120 copolymers of ethylene, olefine and carbon oxides, and phenol formaldehyde resins or urea formaldehyde resins reacted with alkylene  
125 oxides may also be used. A certain proportion

of low molecular weight polyhydroxyl compounds e.g. of the type already mentioned above or of water, aldimines and ketimines may also be included.

- 5 Foam production itself is carried out by known processes at room temperature or at elevated temperatures, simply by mixing the polyisocyanate combinations with the compounds which contain hydroxyl and/or carbonyl groups, optionally adding water, catalysts, emulsifiers and other auxiliary substances such as flame-retarding substances and blowing agents. Mechanical devices are advantageously used for this purpose, e.g. those described in French Patent Specification No. 1,074,713.

- 20 Numerous suitable flame retarding substances are known in the art. These generally contain phosphorus and halogens. Compounds of antimony, bismuth or boron may also be used. A summary of known and suitable flame retarding agents is given in the chapter "Flammhemmende Substanzen", pages 110-111 of *Kunststoff-Handbuch*, Volume VII, Polyurethane, by Vieweg-Hochtlen, Publishers Carl-Hanser-Verlag, Munich 1966. The flame retarding substances are generally added in quantities of from 1 to 20% by weight, preferably from 1 to 15% by weight, based on the quantity of polyisocyanate combinations used.

- 35 Suitable blowing agents include e.g. alkanes, haloalkanes or low boiling solvents in general, e.g. methylene chloride, monofluorotrichloromethane, difluorodichloromethane, acetone or methyl formamide. Compounds which liberate gases at elevated temperatures, such as azo compounds or diurethanes or bis-semi-acetals obtained from two mols of formaldehyde and one mol of ethylene glycol may also be used as blowing agents.

- 45 Suitable activators include e.g. tertiary amines such as triethylamine, dimethylbenzylamine, tetramethylethylene diamine, N-alkyl morpholines, endo-ethylene piperazine, urotropine, hexahydrotriazines such as trimethyl hexahydrotriazine, 2,4,6-dimethylaminomethyl phenol or organic metal salts such as stannous acylates, e.g. stannous salts of 2-ethyl caproic acid, dialkyl stannic acylates such as dibutyl tin dilaurate, or acetyl acetates of heavy metals, e.g. of iron.

- 50 Examples of suitable emulsifiers include hydroxy ethylated phenols, higher sulphonic acids, sulphonated castor oil, hydroxyethylated castor oil, sulphonated ricinoleic acid and ammonium salts of oleic acid. Suitable foam stabilisers include e.g. those based on polysiloxane-polyalkylene glycol copolymers or basic silicone oils. Other suitable emulsifiers, catalysts and additives are mentioned e.g. in "Polyurethanes, Chemistry and Technology", Volumes I and II, Saunders-Frisch, Interscience Publishers, 1962 and 1964.

- 65 The quantities of polyisocyanate solutions

containing biuret polyisocyanates used should generally be at least equivalent to the sum of reactive hydrogen atoms present, but, if desired, they may be used in excess or in sub-equivalent amounts. When producing foams with water as blowing agent, the polyisocyanates will be used in an excess corresponding to the water content. Excess amounts of isocyanates may also be incorporated into the foam as isocyanurate groups, uretdione groups and/or carbodiimide groups in the course of the foaming process by the addition of trivalent or pentavalent phosphorus compounds such as phospholidines, phospholine oxides, tertiary esters, amides or ester amides of phosphorous or phosphoric acid.

The foam resins produced from polyisocyanates which contain biuret groups are widely used, e.g. in the building industry as building panels, sandwich elements, ceiling panels, parapet panels, for heat insulation in refrigerators, refrigerating store rooms, refrigerator cars and cooling containers, in road and railway building, for the technical insulation of pipes, for the insulation of fuel depots, in ship building, as air filters and filters for hydrocarbons in internal combustion engines, as shock absorbing packaging material and as cushioning material.

The following Examples illustrate the invention.

#### Example 1

- a) 2061 g of N-methyl aniline are reacted with 30,000 g of a mixture of 65% of 2,4- and 35% of 2,6-toluylene diisocyanate at 130°C, the amine being added within such a length of time that the temperature does not rise above 160°C (from 1 to 2 hours). The reaction mixture is thereafter heated for one further hour at 150°C. An isocyanate mixture having an NCO content of 40.2% is obtained.
- b) 100 g of an addition product of 90% of propylene oxide and 10% of ethylene oxide with trimethylol propane, average molecular weight 3000, 3 g of water, 1 g of a commercial polyether polysiloxane (e.g. L 540 of Union Carbide Corp.) and 0.4 g of stannous octoate are vigorously mixed with 481 g of products obtained according to Example 1a). A soft polyurethane foam having a density of 36 kg/m<sup>3</sup>, a tensile strength of 1.0 kg.wt/cm<sup>2</sup>, elongation at break of 280%, and compression resistance at 40% compression of 34 g.wt/cm<sup>2</sup> is obtained.

#### Example 2

- a) 2061 g of N-methyl aniline are reacted with 30,000 g of a mixture of 80% of 2,4- and 20% of 2,6-toluylene diisocyanate as described in Example 1a). An isocyanate mixture having an NCO content of 29.9% and a viscosity of 7.1 cP (25°C) is obtained.
- b) 100 g of an addition product of 90% of

- propylene oxide and 10% of ethylene oxide with trimethylol propane, average molecular weight 3000, 3 g of water, 2 g of a commercial polyether polysiloxane (e.g. L 540 of Union Carbide Corp.), 0.7 g of a tertiary amine and 0.1 g of a stannous octoate are vigorously mixed with 40.1 g of the product obtained according to Example 2a). A soft polyurethane foam having a density of 34 kg/m<sup>3</sup>, tensile strength of 0.9 kg.wt/cm<sup>2</sup>, elongation at break of 290% and compression strength at 40% compression of 16 g.wt/cm<sup>2</sup> is obtained.

### Example 3

- 15 a) 2770 g of diphenylamine are reacted with 30,000 g of a mixture of 65% of 2,4- and 35% of 2,6-toluylene diisocyanate as described in Example 1a). An isocyanate mixture having an NCO content of 40.0% (25°C) is obtained.
- 20 b) 100 g of an addition product of 90% of propylene oxide and 10% of ethylene oxide with trimethylol propane, average molecular weight 3000, 3 g of water, 1 g of a commercial polyether polysiloxane (e.g. L 540 of Union Carbide Corp.), 0.5 g of a tertiary amine and 0.3 g of a stannous octoate are vigorously mixed with 48.2 g of the product obtained according to Example 3a). A soft polyurethane foam having a density of 35 kg/cm<sup>3</sup> and a tensile strength of 1.1 kg.wt/cm<sup>2</sup>, an elongation at break of 205% and a compression strength at 40% compression of 32 g.wt/cm<sup>2</sup> is obtained.

### Example 4

- 35 a) 165 g of dibutylamine are reacted with 2000 g of a mixture of 65% of 2,4- and 35% of 2,6-toluylene diisocyanate as described in Example 1a). An isocyanate mixture having an NCO content of 40.1% is obtained.
- 40 b) 100 g of an addition product of 90% of propylene oxide and 10% of ethylene oxide with trimethylol propane, average molecular weight 3000, 3 g of water, 1 g of a commercial polyether polysiloxane (e.g. L 540 of Union Carbide Corp.), 0.5 g of a tertiary amine and 0.5 g of a stannous octoate were vigorously mixed with 48.0 g of the product prepared under 4a). A soft polyurethane foam having a density of 35 kg/m<sup>3</sup>, a tensile strength of 1.2 kg.wt/cm<sup>2</sup>, elongation at break of 260% and compression strength at 40% compression of 35 g.wt/cm<sup>2</sup> is obtained.

### Example 5

- a) 2445 g of diethylamine are reacted with 30,000 g of a mixture of 80% of 2,4- and 20% of 2,6-toluylene diisocyanate as described in Example 1a). An isocyanate mixture having an NCO content of 35.5% is obtained.
- b) 102 g of the products described in Example 5a) are vigorously mixed with 100 g of a product obtained from a sorbitol polyether of OH number 480, 0.8 g of endoethylene piperazine, 1 g of silicone stabiliser (e.g. Sf. 1109 of General Electric) and 40 g of monofluorotrichloromethane. A hard polyurethane foam which has the following physical properties is obtained:—

Density	28 kg/m <sup>3</sup>	
compression strength	2.1 kg.wt/cm <sup>2</sup>	
Heat bending resistance	110°C	70

The foam is dimensionally stable at -30°C and at +100°C.

- c) 40 Parts by weight of a product of addition of propylene oxide to trimethylol propane (OH number 650), 60 parts by weight of a product of addition of 87% propylene oxide and 13 parts by weight of ethylene oxide to propylene glycol (molecular weight approximately 4000) which has been grafted with 4.8 parts by weight of styrene and 19.2 parts by weight of acrylonitrile with the addition of azo diisobutyronitrile (viscosity at 25°C=4200 cP, OH number=12), 1 part by weight of silicone stabiliser (Bk 400 of Goldschmidt AG), 2 parts by weight of N - methyl-N' - (N,N - dimethylaminoethyl) - piperazine and 8 parts by weight of monofluorotrichloromethane are mixed and the mixture is vigorously stirred for 10 seconds with 71 parts by weight of a polyisocyanate which is prepared according to Example 5a) (from 3122 g of diethylamine and 30,000 g of a mixture of 80% of 2,4- and 20% of 2,6-toluylene diisocyanate) (viscosity at 25°C=10 cP, NCO=32%). The mixture is introduced into a metal mould which has been heated to 60°C (dimensions of moulded part 300×300×10 mm). The reaction starts after 30 seconds and the reaction mass foams up. The reaction product gels after a further 20 seconds. After 5 minutes, the moulded product is removed from the mould. It has an overall apparent density of 0.707 g/cm<sup>3</sup> and a solid marginal zone on both sides.

Mechanical properties of the synthetic resins product:

	Flexural strength according to DIN 53 423	$\delta_{bB}=260 \text{ kg.wt/cm}^2$
110	Elastic modulus from bending test	$E_b=6800 \text{ kg.wt/cm}^2$
	Practical dimensional stability at elevated temperature under bending stress according to DIN 53 424, bending stress approximately	
115	at a deflection of 10 mm	$3 \text{ kg.wt/cm}^2$ $HB_{10}=82^\circ\text{C}$

## Example 6

a) 1766 g of a crude toluylene diisocyanate of NCO content 39%, are reacted with 73 g of diethylamine as described in Example 1a).

5 A polyisocyanate which has an NCO content of 33.7% and a viscosity of 1047 cP (25°C) is obtained.

b) 104 g of the polyisocyanate described in Example 6a) are thoroughly mixed with 100 g of a propylene oxide polyether of OH number 470 which has been started with sorbitol, 1 g of methylene diamine, 1 g of silicone stabiliser (Sf 1109 of General Electric) and 40 g of monofluorotrichloromethane. A hard polyurethane foam resin which has the following physical properties is obtained:

Unit weight 25 kg/m<sup>3</sup>  
 Compression strength 2.5 kg.wt/cm<sup>2</sup>  
 Resistance to bending at elevated temperature 130°C

The foam resin is dimensionally stable at -30°C and at +100°C.

## Example 7

a) A mixture of 101.3 g of diethylamine and 24.95 g of water is added dropwise at 80°C to 1700 g of 2,4-tolylene diisocyanate. The resulting suspension is then heated to 175°C for one hour, the precipitate going into solution. A polyisocyanate which has an NCO content of 31.5% and a viscosity of 1137 cP (at 25°C) is obtained.

b) 115 g of the polyisocyanate prepared in Example 7a) are vigorously mixed with 100 g of a propylene oxide polyether of OH number 470 which has been started with sorbitol, 0.8 g of triethylene diamine endoethylene piperazine, 1 g of silicone stabiliser (Sf 1109 of General Electric) and 40 g of monofluoro-

trichloromethane. A hard polyurethane foam which has the following physical properties is obtained:

Unit weight 26 kg/m<sup>3</sup>  
 Compression strength 2.9 kg.wt/cm<sup>2</sup>  
 Resistance to bending at elevated temperature 142°C

The foam resin is dimensionally stable at -30°C and at +100°C.

c) 40 Parts by weight of an addition product of propylene oxide and trimethylol propane (OH number 650), 60 parts by weight of the product of addition of 84% propylene oxide and 13 parts by weight of ethylene oxide to propylene glycol (molecular weight approximately 4000) which has been grafted with 4.8 parts by weight of styrene and 19.2 parts by weight of acrylonitrile with the addition of azo diisobutyronitrile (viscosity at 25°C=4200 cP, OH number=12), 1 part by weight of silicone stabiliser (B 1400 of Goldschmidt AG), 2 parts by weight of N - methyl - N' - (N,N - dimethylaminoethyl) - piperazine and 8 parts by weight of monofluorotrichloromethane are mixed, and the mixture is vigorously stirred together for 10 seconds with 74 parts by weight of the polyisocyanate prepared according to Example 7a) (viscosity at 25°C=1137 cP, NCO=31.4%). The mixture is introduced into a metal mould (300×300×10 mm) heated to 60°C. The reaction starts after 30 seconds, the reaction mass foaming up. The reaction product gels after a further 20 seconds. The moulded product is removed from the mould after 5 minutes. It has an overall apparent density of 0.66 g/cm<sup>3</sup> and a dense marginal zone on both sides.

Mechanical properties of the synthetic resin produced:

Flexural strength according to DIN 53 423  $\delta_{bB}=265 \text{ kg.wt/cm}^2$   
 Elastic modulus from bending test  $E_b=6800 \text{ kg.wt/cm}^2$   
 Practical dimensional stability at elevated temperature under bending stress in accordance with DIN 53 424, flexural stress approximately 3 kg/wt/cm<sup>2</sup> at 10 mm deflection:  $HB_{10}=102^\circ\text{C}$

d) 100.0 Parts by weight of a polypropylene glycol which has been started with trimethylol propane and which has been modified with ethylene oxide to result in approximately 60% of primary hydroxyl groups in the end positions at an OH number of 35.0, 2.5 parts by weight of water, 0.2 part by weight of methylene diamine and 2.0 parts by weight of dimethylbenzylamine are mixed together and

reacted with 38.9 parts by weight of a mixture of 2,4- and 2,6-tolylene diisocyanate which has been modified with water/diethylamine (2:1) as in Example 7a) and which contains 80% of 2,4- and 2,6-tolylene diisocyanate (NCO content 40.55%, viscosity at 25°C 22 cP).

A foam resin which has the following mechanical properties is obtained:

	Density according to DIN 53 420	50 kg/m <sup>3</sup>	of water, 0.2 part by weight of methylene diamine, 1.5 parts by weight of triethylamine and 1.0 part by weight of a polyglycol ether of oleic acid amide are mixed together and reacted with 57.0 parts by weight of the polyisocyanate prepared in Example 10a).	55
5	Tensile strength according to DIN 53 571	0.8 kg.wt/cm <sup>2</sup>	A foam resin which has the following mechanical properties is obtained:	
	Elongation at break according to DIN 53 571	130%		
10	Pressure test at 40% compression according to DIN 53 577	30 g.wt/cm <sup>2</sup>	Density according to DIN 53 420	60
			47 kg/m <sup>3</sup>	
	e) 100 Parts by weight of polypropylene glycol of hydroxyl number 35 which has been started with trimethylol propane and which has been modified with ethylene oxide to result in approximately 60% of primary hydroxyl groups in end positions, 36.5 parts by weight of the polyisocyanate used in Example 7d), 2.5 parts by weight of water and 0.5 part by weight of an amine catalyst such as tetramethyl guanidine were thoroughly mixed. The resulting foam resin is self-extinguishing according to ASTM.		Tensile strength according to DIN 53 571	65
15			0.9 kg.wt/cm <sup>2</sup>	
			Elongation at break according to DIN 53 571	150%
20			Pressure test at 40% compression according to DIN 53 577	27 g.wt/cm <sup>2</sup>
	Example 8		Example 11	70
25	169 g of diethylamine are reacted with 1823 g of hexamethylene diisocyanate as described in Example 1a). An isocyanate mixture having an NCO content of 35.6% and a viscosity of 12 cP (at 25°C) is obtained.		a) 111.5 g of N,N'-diethyl-4,4'-diaminodiphenylmethane are reacted with 1000 g of 4,4'-diphenylmethane diisocyanate as described in Example 10a). A polyisocyanate having an NCO content of 25.3% and a viscosity of 800 cP (25°C) is obtained.	75
	Example 9		b) 50 Parts by weight of a product of addition of propylene glycol to trimethylol propane (OH number=650), 20 parts by weight of a product of addition of propylene oxide to triisopropanolamine (OH number=290), 30 parts by weight of a product of addition of ethylene oxide/propylene oxide to trimethylol propane (OH number=28), 1 part by weight of silicone stabiliser B 1500 of Goldschmidt AG, 2 parts by weight of N - methyl - N'-(N,N - dimethylaminoethyl) - piperazine and 8 parts by weight of monofluorotrichloromethane are mixed together and the mixture is thoroughly stirred together for 10 seconds with 147 parts by weight of the polyisocyanate prepared in Example 11a) (viscosity at 25°C=800 cP, NCO=25.3%). The mixture is introduced into a metal mould (300×300×10 mm) which has been heated to 60°C. The reaction starts after 40 seconds, the reaction mass foaming up. The reaction product gels after a further 40 seconds.	80
30	255 g of piperidine are reacted with 2451 g of hexamethylene diisocyanate as described in Example 1a). An isocyanate mixture having an NCO content of 34.35% is obtained.		The moulded product is removed from the mould after 5 minutes. It has an overall apparent density of 0.640 g/cm <sup>3</sup> and a dense marginal zone on both sides.	85
	Example 10		Mechanical properties of the synthetic resin produced:	90
35	a) 73 g of diethylamine are added dropwise to 1470 g of 4,4'-diphenylmethane diisocyanate at 80°C. The resulting suspension is then heated at 170°C for 3 hours, the precipitate going into solution. After cooling and filtration, an isocyanate mixture having an NCO content of 26.9% and a viscosity of 126 cP (at 25°C) is obtained. In contrast to 4,4'-diphenylmethane diisocyanate, which crystallises well, the reaction product remains liquid at room temperature.			95
40	b) 100.0 Parts by weight of a polypropylene glycol which has been started with trimethylol propane and which has been modified with ethylene oxide to result in approximately 65% of primary hydroxyl groups in end positions at an OH number of 35.0, 2.5 parts by weight			
45				
50				
105	Flexural strength according to DIN 53 423		$\delta_{bb}=335 \text{ kg.wt/cm}^2$	
	Elastic modulus from bending test		$E_b=8800 \text{ kg.wt/cm}^2$	
	Practical dimensional stability at elevated temperature under bending stress in accordance with DIN 53 424, flexural stress approximately 3 kg/wt/cm <sup>2</sup> at 10 mm deflection:		$HB_{10}=111^\circ\text{C}$	
110				



## Example 12

- a) 75.3 g of N,N'-dimethyl-4,4'-diamino-diphenylmethane are reacted with 1440 g of a crude 4,4'-diphenylmethane diisocyanate as described in Example 10a). A polyisocyanate which has an NCO content of 26.75%, and a viscosity of 660 cP (25°C) is obtained.
- b) 125 g of the polyisocyanate described in Example 12a) are thoroughly mixed with 100 g of a propylene oxide polyether of OH number 470 which has been started with sorbitol, 1 g of methylene diamine, 1 g of silicone stabiliser (Sf 1109 of General Electric) and 50 g of monofluorotrichloromethane. A hard polyurethane foam resin which has the following physical properties is obtained:

Unit weight	26 kg/m <sup>3</sup>
Compression strength	2.0 kg.wt/cm <sup>2</sup>
Resistant to bending at elevated temperature	115°C

## Example 13

- a) 131 g of N,N'-diethyl-4,4'-diamino-diphenylmethane are reacted with 1000 g of a mixture of 80% of 2,4- and 20% of 2,6-toluylene diisocyanate as described in Example 1a). A polyisocyanate which has an NCO content of 38.0% and a viscosity of 29 cP (at 25°C) is obtained.
- b) 100.0 Parts by weight of a polypropylene glycol which has been started with trimethylol propane/hexanetriol and has been modified with ethylene oxide to result in approximately 65% of primary hydroxyl groups in end positions at an OH number of 35, 2.5 parts by weight of water, 0.2 part by weight of methylene diamine, 1.5 parts by weight of triethylene and 2.5 parts by weight of a polypropylene glycol of OH number 380 which has been started with trimethylol propane are mixed together and reacted with 41.5 parts by weight of the polyisocyanate described in Example 13a).

A foam resin which has the following mechanical properties is obtained:

Unit weight according to DIN 53 420	45 kg/m <sup>3</sup>
Tensile strength according to DIN 53 571	0.7 kg.wt/cm <sup>2</sup>
Elongation at break according to DIN 53 571	125%
Pressure test at 40% compression according to DIN 53 577	31 g.wt/cm <sup>2</sup>

## WHAT WE CLAIM IS:—

1. A process for the preparation of liquid polyisocyanates which contain biuret groups which comprises reacting amines and polyisocyanates, in which the polyisocyanates are reacted at a temperature of from 80 to 200°C with secondary amines at an NCO/NH ratio of from 4:1 to 100:1.
2. A process as claimed in claim 1 in which the NCO/NH ratio is from 6:1 to 40:1.
3. A process as claimed in claim 1 or claim 2 in which the temperature is from 130 to 170°C.
4. A process as claimed in any of claims 1 to 3 in which the process is carried out continuously or adiabatically.
5. A process as claimed in any of claims 1 to 4 in which the secondary amines are secondary monoamines.
6. A process as claimed in any of claims 1 to 4 in which the secondary amines are bis-secondary diamines.
7. A process as claimed in any of claims 1 to 6 in which the polyisocyanates are diisocyanates.
8. A process for the preparation of liquid polyisocyanates where contain biuret groups substantially as herein described with reference to the Examples.
9. Liquid polyisocyanates which contain biuret groups.
10. A liquid polyisocyanate as claimed in claim 9 which is in the form of a solution in a polyisocyanate which is free from biuret groups when prepared by a process as claimed in any of claims 1 to 8.
11. A process for the production of polyurethane foam resins by the isocyanate polyaddition process in which the isocyanate components are biuret-containing polyisocyanates as claimed in claim 9 or claim 10.
12. A process for the production of polyurethane foam resins substantially as herein described with reference to the Examples.
13. Polyurethane foam resins when prepared by a process as claimed in claim 11 or claim 12.

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